Ionic solutions under high pressures VI : mobilities and hydration of monocarboxylate ions

AUTHOR(S):

Nakahara, Masaru; Osugi, Jiro

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Mobilities and Hydration of Monocarboxylate Ions*

BY MASARU NAKAHARA AND JIRO OSUGI

The electrical conductivities of potassium acetate, propionate and butyrate in water were measured in the concentration range 10^{-4} to 10^{-3} N up to 5,000 atm at 25°C. The equivalent conductivity at infinite dilution of each salt is obtained by means of Onsager's limiting equation and then separated into the limiting ionic equivalent conductivities by using the conductivity[1] and transference number[2] data for potassium chloride.

According to the same line, the equivalent conductivities of the bulky monovalent ions studied till now by the authors are recalculated. The plot of the limiting ionic equivalent conductivity against pressure at 25°C has a maximum for acetate and propionate ions as seen in the case of simple monatomic ions, but no maximum for perchlorate, tetraalkylammonium and butyrate ions. The Walden product has a small positive derivative with respect to pressure at 1 atm only for acetate ion and negative one for all the other ions. The negative sign of the pressure coefficient of the Walden product is interpreted in terms of the higher density of water in the hydration shell than in the bulk. It is also pointed out that the compression of hydrated ions with the application of pressure is a factor of great importance that makes the Walden product increase with increasing pressure.

Introduction

Various kinds of thermodynamic investigations on aqueous solutions of carboxylate salts have been done at atmospheric pressure : Smith and Robinson[3] measured the activity coefficients, by which the presence of micelle formation is indicated in all the solutions from six- to ten-carbon atom salt ; Ackermann and Schreiner[4] determined the partial molal heat capacities; Snell and Greyson[5] studied the entropies of transfer between heavy and normal water in the dilute solutions, which change from negative to positive values in passing from sodium formate to sodium caproate ; Lindenbaum[6] estimated the apparent molal heat contents, and the osmotic and activity coefficients ; Millero[7] tabulated the conventional partial molal volumes of caboxylate ions.

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3) E. R. B. Smith and R. A. Robinson, *Trans. Faraday Soc.*, **38**, 70 (1942)
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Most of these experiments were carried out to cast light on the specific nature of the interaction between alkyl chain and water molecules. There have been gathered many thermochemical data which suggest anomalously strong interaction between water molecules and hydrocarbon chain, although thermodynamics can say nothing conclusive in the molecular level without a reliable model or assumption.

Transport properties, such as viscosity, ionic conductivity and relaxation time, also can give insight into the intermolecular interactions in pure water or aqueous ionic solutions. Previously,[8,9] the authors reported the effect of pressure on the mobilities and hydration of symmetrical tetraalkylammonium ions. Now, we have measured the electrical conductivities of carboxylate salts in water at high pressure as an extension of the study on the interaction between water and organic ions. The electrical conductivities of carboxylate salts have been already measured at high pressures by Hamann and his coworkers[10], Ellis and Anderson[11], Lown *et al.*,[12] Suzuki *et al.*[13] and Hφiland[14], to determine the volumes of ionization or dimerization of carboxylic acids in water. However, the equivalent conductivities of carboxylate ions at infinite dilution at high pressure have not yet been reported, which are given here to clarify the interaction between hydrocarbon chain ond water, the so-called hydrophobic hydration.

Experimental

Potassium salts of acetate, propionate and *n*-butyrate, CH_3CO_2K, $C_2H_5CO_2K$ and $C_3H_7CO_2K$ of guaranteed reagent grade were supplied by Nakarai Chemicals Co., Ltd. Acetate salt was recrystallized three times from methanol solution by adding chilled ethyl ether and then heated at 160°C for 14 hr to a constant weight. Propionate salt was recrystallized three times from methanol solution. The purified crystal was dried in vacuum at room temperature for a week and then heated at 160°C for 11 hr. Butyrate salt was recrystallized three times from ethanol solution, dried in vacuum at room temperature for two days and heated at 100°C for 8 hr.

All the experimental procedures and apparatuses used are the same as in the previous comunications.

Results and Discussion

Determination of $\Lambda^{\circ(p)}$ from $\Lambda^{(p)}$

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There are the following ways to determine the equivalent conductivity at infinte dilution at high pressure from the observed values of equivalent conductivities, $\Lambda^{(p)}$. 1) The Kohlrausch plot of Λ *vs.* $\sqrt{C}$ can be used for the extrapolation at high pressure, as well as at atmospheric pressure. 2) Gancy and Brummer[15] showed the plot of $\Lambda^{(p)}/\Lambda^{(1)}$ against $\sqrt{C}$ was very convenient. 3) The authors[1,8,9] pointed out that the Onsager equation of conductivity was applicable to dilute solutions at high pressure. 4) For the solutions of moderate concentration, $\Lambda^{\circ(p)}$ can be more accurately determined by the Fuoss-Onsager equation programed for a rapid electronic computer. The first two methods are only empirical, and the last two are based on the theoretical equations where the viscosity and dielectric constant of solvent are required at high pressure. When the electrolyte solution is strong and sufficiently dilute ($<10^{-3}$ N) as in the present case, the difference between the value of $\Lambda^{\circ(p)}$ calculated by

Table 1 $\Lambda^{\circ(p)}(CH_3COOK)$, $ohm^{-1}\cdot cm^2\cdot equiv^{-1}$, at 25°C

Pressure, atm \ Sample*	A	B	C	D	Average
1	114.4	114.4	114.4	114.3	114.4
500	115.7	115.5	115.6	115.3	115.5
1,000	115.4	115.2	115.3	114.9	115.2
1,500	113.9	113.9	114.1	113.9	114.0
2,000	111.9	112.0	112.1	112.0	112.0
2,500	109.2	109.3	109.6	109.5	109.4
3,000	106.7	106.7	106.8	106.8	106.8
3,500	103.7	103.6	103.9	103.7	103.7
4,000	100.5	100.5	100.5	100.6	100.5
4,500	97.3	97.2	97.3	97.4	97.3
5,000	93.9	93.9	94.0	94.2	94.0

* A: 3.995×10^{-4} N, B: 6.393×10^{-4} N, C: 7.991×10^{-4} N, D: 10.388×10^{-4} N at 1 atm

Table 2 $\Lambda^{\circ(p)}(C_2H_5COOK)$, $ohm^{-1}\cdot cm^2\cdot equiv^{-1}$, at 25°C

Pressure, atm \ Sample*	A	B	C	D	Average
1	109.3	109.2	109.3	109.3	109.3
500	109.9	109.8	110.0	109.9	109.9
1,000	109.5	109.4	109.7	109.6	109.6
1,500	108.4	108.1	108.1	108.5	108.3
2,000	106.3	106.2	106.3	106.3	106.3
2,500	104.1	104.0	103.9	104.0	104.0
3,000	101.4	101.3	101.4	101.4	101.4
3,500	98.7	98.4	98.6	98.6	98.6
4,000	95.7	95.5	95.6	95.7	95.6
4,500	92.6	92.5	92.6	92.7	92.6
5,000	89.5	89.5	89.6	89.7	89.6

* A: 3.955×10^{-4} N, B: 6.327×10^{-4} N, C: 8.700×10^{-4} N, D: 11.073×10^{-4} N at 1 atm

Table 3 $\Lambda^{\circ(p)}(C_3H_7COOK)$, $ohm^{-1}\cdot cm^2\cdot equiv^{-1}$, at 25°C

Pressure, atm \ Sample*	A	B	C	D	Average
1	106.0	105.9	105.9	106.0	106.0
500	106.5	106.2	106.3	106.2	106.3
1,000	106.2	105.5	105.7	105.7	105.8
1,500	104.9	104.4	104.4	104.3	104.5
2,000	102.8	102.4	102.4	102.6	102.5
2,500	100.3	100.0	100.1	100.6	100.3
3,000	97.4	97.5	97.3	97.7	97.5
3,500	94.9	94.6	94.4	94.8	94.7
4,000	92.1	91.7	91.6	91.8	91.8
4,500	89.0	88.8	88.7	88.7	88.8
5,000	86.0	85.9	85.6	85.6	85.8

* A: 4.514×10^{-4} N, B: 6.771×10^{-4} N, C: 9.027×10^{-4} N, D: 11.277×10^{-4} N at 1 atm

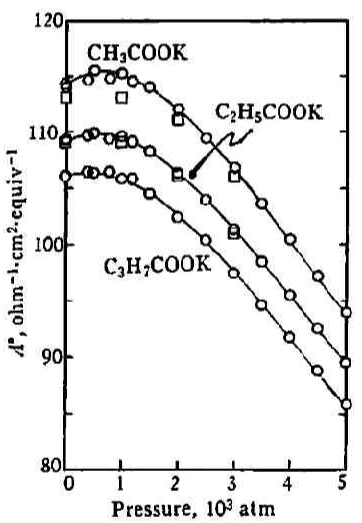

Fig. 1 Pressure dependence of the limiting equivalent conductivities of potassium carboxylates at 25°C
○: present work, □: Ref. 1), ○: Ref. 14)

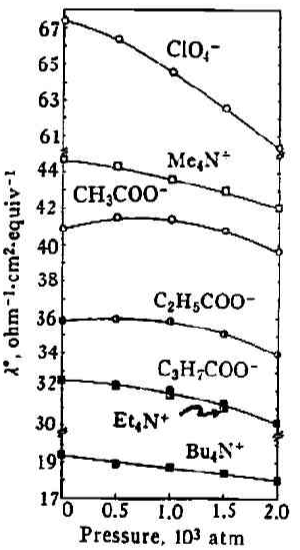

Fig. 2 Pressure dependence of the limiting equivalent conductivities of some bulky monovalent ions at 25°C

the method 4) and that by the method 3) does not exceed the experimental uncertainty (*ca.* ±0.3 in Λ units). Hence, the values of $\Lambda^{\circ(p)}$ of potassium carboxylates are calculated according to the method 3) and listed in Tables 1~3. The obtained values of $\Lambda^{\circ(p)}$ of potassium acetate, propionate and butyrate are compared with the literature values in Fig. 1. In the cases of CH_3CO_2K and $C_2H_5CO_2K$ there is a weak tendency that the authors'>Høiland's>Hamann's. However, discrepancies are not very

Table 4 Ionic equivalent conductivities, $ohm^{-1}\cdot cm^2\cdot equiv^{-1}$, at infinite dilution at 25°C

Pressure, atm \ Ion	K^+	Me_4N^+	Et_4N^+	Bu_4N^+	Cl^-	ClO_4^-	$CH_3CO_2^-$	$C_2H_5CO_2^-$	$C_3H_7CO_2^-$
1	73.5	44.7	32.5	19.4	76.4	67.4	40.9	35.8	32.5
500	74.0	44.3	32.3	18.9	78.6	66.4	41.5	35.9	32.3
1,000	73.8	43.6	31.7	18.7	79.6	64.6	41.4	35.8	32.0
1,500	73.2	43.0	31.0	18.4	79.7	62.6	40.8	35.1	31.3
2,000	72.3	42.1	30.2	18.0	79.3	60.3	39.7	34.0	30.2

large in every case.

Obtaining of $\lambda^\circ(p)$ from $\Lambda^\circ(p)$

The single-ion equivalent conductivities at infininite dilution can be given by the two independent observations, conductivities and transference numbers. The transference number is defined as

$$t^\circ(p)=\lambda^\circ(p)/\Lambda^\circ(p). \qquad (1)$$

In the present calculation the conductivity of KCl measured by the authors[8] and the transference number of K^+ in KCl by Kay *et al.*[2] are chosen to obtain by Eq. (1) the equivalent conductivities of K^+ and Cl^- ions up to 2,000 atm (1 atm$=1.013\times10^5$ Pa). Then, according to the Kohlrausch law of independent migration of ions, we have

$$\lambda^\circ(p)(RCOO^-)=\Lambda^\circ(p)(RCOOK)-\lambda^\circ(p)(K^+). \qquad (2)$$

and

$$\lambda^\circ(p)(R_4N^+)=\Lambda^\circ(p)(R_4NCl)-\lambda^\circ(p)(Cl^-). \qquad (3)$$

The values of $\lambda^\circ(p)$ of carboxylate, tetraalkylammonium[8,9] and other ions obtained in this way are given in Table 4. and plotted against pressure in Fig. 2. It is to be noted that the tetraalkylammonium, perchlorate and *n*-butyrate ions do not have a maximum in the plot of λ° against pressure, although the viscosity of water against pressure has a maximum at about 500 atm at 25°C, which may be a possible evidence for the water structure and structure-breaking effect of pressure. It is also noticeable that in the homologuous series of the carboxylate ions the lower two homologues have a minimum in the λ° *vs.* pressure plot like simple monatomic ions, such as alkali metal and halide ions. The carboxylate ion $RCOO^-$ consists of the two functional groups, the nonpolar alkyl chain R and the ionic carboxyl group COO^-. If we assume that the interaction between R and water and that between COO^- and water are independent, we can conclude that the interaction between R and water (the so-called hydrophobic hydration) makes the maximum disappear in the plot of λ° of butyrate ion against pressure at 25°C. For the same reason, probably, all the tetraalkylamonium ions shown in Fig. 2 have no maximum. Furthermore, it is interesting that ClO_4^- ion which is often called a strong structure-breaker also has no maximum. It may be accounted for by assuming that water structure in the vicinity of ClO_4^- ion collapses and the structure-broken water which tends to behave like a normal liquid mainly controls the mobility of ClO_4^- ion.

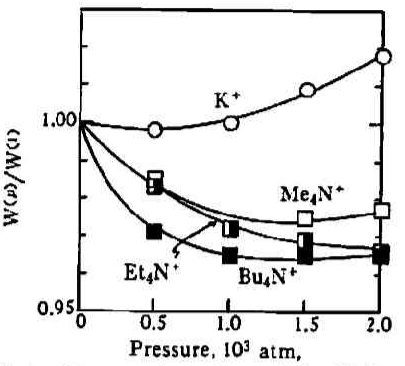

Fig. 3 Pressure dependence of the Walden products of some cations at 25°C

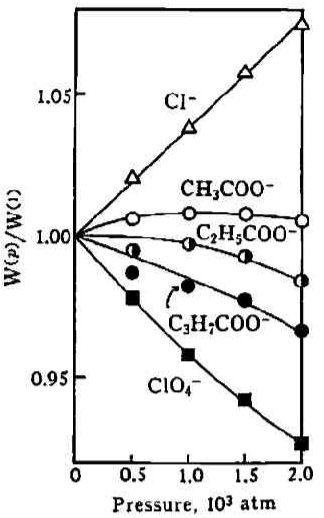

Fig. 4 Pressure depeddance of the Walden products of some anions at 25°C

At the end of the last century, Tammann[16] pointed out a parallelism betwen the pressure dependence of the electrical conductivities (κ or Λ) of aqueous electrolyte solutions and that of the water fluidity, and in the 1950's Hamann[10] made more precise comparison between Λ° and $1/\eta^\circ$ (η°: viscosity of water) at high pressure. In a rigorous sense, however, there is no exact correspondence between λ° and $1/\eta^\circ$, especially in the cases of such bulky polyatomic monovalent ions as $RCOO^-$, R_4N^+ and ClO_4^-.

Pressure dependence of the Walden product

Owing to the undeveloped stage of the theory for λ°, we can not expect any thoroughly quantitative explanation of the pressure or temperature dependence of the ionic Walden product, $W=\lambda^\circ\cdot\eta^\circ$ as yet. Then, we want to attempt some qualitative discussion of the pressure dependence of W by proposing a new method.

It may be approximated that water exists in the following two states; that is

$$\begin{array}{ccc}\text{state I} & K & \text{state II}\\ \text{water} & \rightleftarrows & \text{water}\\ \text{in the bulk} & & \text{in the hydration shell}\end{array} \qquad (3)$$

The equilibrium constant K can be expressed as

$$K=\frac{a_{II}}{a_I}=\frac{hm}{55.5-hm}\frac{\gamma_{II}}{\gamma_I}\fallingdotseq\frac{hm}{55.5}\frac{\gamma_{II}}{\gamma_I}\ (m\ll 1), \qquad (4)$$

where a is the activity of water in each state, γ its activity coefficient, h the hydration number of an ion at infinite dilution and m the concentration of the ion in 1 kg water which is arbitrarily very small. When the logarithmic form of Eq. (4) is combined with the fundamental thermodynamic equation,

16) G. Tammann, *Z. Phys. Chem.*, **17**, 725 (1895)

$$RT \ln K = -\Delta\overline{G}^{\circ}, \tag{5}$$

it gives

$$\ln (hm) + \ln (\gamma_{II}/\gamma_{I}) - \ln 55.5 = -\Delta\overline{G}^{\circ}/(RT). \tag{6}$$

If we differentiate Eq. (6) with respect to pressure, neglecting the pressure dependence of $\ln(\gamma_{II}/\gamma_{I})$, we have

$$\frac{1}{h}\left(\frac{\partial h}{\partial P}\right)_T = -\frac{V_{II}^{\circ} - V_{I}^{\circ}}{RT}, \tag{7}$$

where V_{II}° and V_{I}° are the molar volumes of water in the respective states. From Eq. (7), we will be able to know the density in the hydration shell, if we are well informed about h as a function of pressure by NMR *etc.* At present, however, h is not known exactly at high pressure, and then we here try to develop an approximate analysis to know only the sign of $(\partial h/\partial P)_T$ in the left-hand side of Eq. (7), which gives

$$\text{sign of } \left(\frac{\partial h}{\partial P}\right)_T = -\text{sign of } (V_{II}^{\circ} - V_{I}^{\circ}). \tag{8}$$

The Stokes-Einstein equation

$$\lambda^{\circ} \cdot \eta^{\circ} = \frac{|z| eF}{6\pi r_s}, \tag{9}$$

where z, e, F and r_s are respectively the ionic valence, protonic charge, Faraday constant and Stokes radius, may be modified as follows:

$$\lambda^{\circ} \cdot \eta^{\circ} = \frac{|z| eF}{C(r_e) \cdot r_e} \quad (\lim_{r_e \to \infty} C(r_e) = 6\pi), \tag{10}$$

where r_e is the effective radius of an ion whose hydration number is h. Here, r_e or h is defined practically by the conductivity measurement. Although the definition of r_e of such chain-like ions as $RCOO^-$ might be somewhat difficult to make, the thermal rotation of ions would make the spherically asymmetric nature disappear effectively, as long as R is not so large. Differentiating the logarithmic form of Eq. (10) with respect to pressure, we have

$$\left(\frac{\partial W}{\partial P}\right)_T = -W\left(\frac{\partial r_e}{\partial P}\right)_T \left\{\frac{1}{r_e} + \frac{1}{C}\left(\frac{\partial C}{\partial r_e}\right)_T\right\}, \tag{11}$$

where the third factor in the right-hand side has a positive value because $(\partial C/\partial r_e)_T$ is positive[17]. Consequently, Eq. (11) gives

$$\text{sign of } (\partial W/\partial P)_T = -\text{sign of } (\partial r_e/\partial P)_T. \tag{12}$$

The effective radius, r_e is a function of pressure and hydration number, h at constant temperature; that is

$$dr_e = \left(\frac{\partial r_e}{\partial P}\right)_{h,T} dP + \left(\frac{\partial r_e}{\partial h}\right)_{P,T} dh, \tag{13}$$

and then we have

17) M. Nakahara, K. Shimizu and J. Osugi, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sec.*), **92**, 785 (1971)

$$\left(\frac{\partial r_e}{\partial P}\right)_T=\left(\frac{\partial r_e}{\partial P}\right)_{h,T}+\left(\frac{\partial r_e}{\partial h}\right)_{P,T}\left(\frac{\partial h}{\partial P}\right)_T. \tag{14}$$

where the first term in the right-hand side is negative and the first factor of the second term is positive. In case the second term in the right-hand side is more important than the first, it follows that

$$\text{sign of } (\partial r_e/\partial P)_T=\text{sign of } (\partial h/\partial P)_T. \tag{15}$$

By combining Eqs.(8), (12) and (15), we arrive at the interesting equation.

$$\text{sign of } (\partial W/\partial P)_T=\text{sign of } (V_{II}^{\circ}-V_I^{\circ}). \tag{16}$$

The Walden products of the ions in Table 4 are plotted in Figs. (3) and (4) by using the viscosity data of water measured by Cappi[18]. As shown in Figs. (3) and (4), the pressure coefficient of the Walden product at 1 atm and at 25°C are negative for K^+, R_4N^+, $C_2H_5COO^-$, $C_3H_7COO^-$ and ClO_4^- ions, and positive for Cl^- and CH_3COO^- ions. When $(\partial W/\partial P)_T$ is negative, $(\partial r_e/\partial P)_T$ is positive from Eq. (12), and then $(\partial h/\partial P)_T$ is positive from Eq. (14). Therefore, Eq. (8) gives

$$V_{II}^{\circ}<V_I^{\circ}, \tag{17}$$

which means that at 1atm the density of water in the hydration shell is larger than that in the bulk of water in the cases of K^+, Me_4N^+, Et_4N^+, Bu_4N^+, $C_2H_5COO^-$, $C_3H_7COO^-$ and ClO_4^- ions. But in the cases of Cl^- and CH_3COO^- ions, it is dangerous to say that the density in the hydration shell is smaller, because the first term in the right-hand side of Eq. (14) is negative and therefore does not decide whether $(\partial h/\partial P)_T$ is negative or not. To interpret the large increase in the Walden products of highly hydrated ions, such as Li^+, Cl^- and other polyvalent ions, with increasing pressure, the compression effect which is manifested in Eq. (14) would be a factor of great importance and not be negligible.

Laboratory of Physical Chemistry
Department of Chemistry
Faculty of Science
Kyoto University
Kyoto 606
Japan

18) J.B. Cappi, Ph. D. Thesis, London University (1964)